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Supramolecular structure and thermal behavior of cassava starch treated by oxygen and helium glow-plasmas

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Abstract: The thermal property of cassava starch was regulated by the oxygen or helium glow-plasma treatment to change its supramolecular hierarchical structure. By investigating the microstructural and mesoscopic scale structural alterations and the thermal transition without and with the glow-plasma treatment, the underlying mechanism was explored through establishing a structure-thermal property relationship. Particularly, while there were negligible changes to the granule morphology, the glow-plasma predominantly disorganized the crystallites with low perfection and thermal stability, resulting in decreased alignment of double-helices within the crystalline lamellae, reduced relative crystallinity and thermal transition enthalpy, and increased transition temperatures accompanied by a narrowed gelatinization temperature range. The thermal transition parameters could be further modulated by simply changing the atmosphere type and treatment time. This is much different from our previous study which showed if glow-plasma disrupted the supramolecular structure of starch, the thermal transition temperatures would be reduced. These findings from present study indicate that the glow-plasma treatment can serve as a highly-safe physical method to rationally regulate the hierarchical structure of cassava starch and thus to realize the development of starch-based products with desired thermal behavior.

Keywords: Cassava starch; Glow-plasma; Supramolecular structure; Thermal property

1. Introduction

Starch is one of the most important raw materials for food and non-food industries (Randzio, Flis-Kabulska, & Grolier, 2003). Starch consists of amylose and amylopectin (Liu, Halley, & Gilbert, 2010). Due to its advantages regarding biodegradability and biocompatibility, starch has gained huge attention as a polymer resource for functional foods, carriers for bioactive components (Hoover, Hughes, Chung, & Liu, 2010; Situ, Li, Liu, & Chen, 2015), and eco-friendly thermoplastics (Mateyawa, et al., 2013; Zhang, et al., 2015b). Nonetheless, the applications of starch-based products may be limited by the inherent characteristics of native starch, such as low solubility (Bemiller, 1997). To improve the performance of starch, physical, chemical and enzymatic techniques have been used to modulate starch structures in terms of the granule integrity, the perfection and amount of crystallites, and the chain structure (Bemiller, 1997; Zhang, Chen, Li, Li, & Zhang, 2015a).

For rational utilization of starch, it is essential to understand its unique supramolecular structure and key properties such as thermal transition. In the starch granule, amylose and amylopectin molecules form a semi-crystalline system, comprised of granule morphology (μm), growth rings (100-400 nm), semi-crystalline lamellae (periodicity, 9-10 nm), and crystallites (nm) (Pikus, 2005a; Zhang, et al., 2015b). The A-, B-, C- and V-type crystalline structures have been confirmed (Buleon, Colonna, Planchot, & Ball, 1998; Kim & Huber, 2010). If starch is heated in water at a temperature higher than a specific value, its granules undergo irreversible swelling and therefore starch gelatinization (thermal transition) is completed, indicated by a heat-induced transformation of the

semi-crystalline structure into a paste. And this transformation is significant for starch applications (Zhang, Zhao, Li, Li, Xie, & Chen, 2014b). Hence, the thermal property of starch is closely related to the supramolecular structure and is crucial for the design of production of starch-based products.

Research has already shown that chemical modification can change the thermal transition of starch. For example, acid-hydrolyzed and oxidized starches have shown to have lower transition temperatures (Singh, Kaur, & McCarthy, 2007). Nevertheless, physical treatment to starch has also attracted great attention due to the concerns over generated wastes and food safety issues resulting from chemical modification of starch. As an eco-friendly physical technique, glow-plasma has been shown to alter the molecular, surface and crystalline structures of starch, resulting in changes to the digestibility and thermal stability (Lii, Liao, Stobinski, & Tomasik, 2002a, 2002b; Zou, Liu, & Eliasson, 2004). Very recently, our findings revealed that the oxygen glow-plasma was more effective at altering the structure of B-polymorphic starch (than those of the A-type starch), as its larger amount of inter-helical water could be induced by the glow-plasma (Zhang, Xiong, Li, Li, Xie, & Chen, 2014a); again, the nitrogen and helium glow-plasmas could reduce the gelatinization temperature of potato starch by inducing structural disorganization. Therefore, the glow-plasma treatment shows great potential as a physical technique for the development of starch-based products.

Cassava starch has been widely used in different industrial products, e.g., foods, feeds, and adhesives (Santisopasri, Kurotjanawong, Chotineeranat, Piyachomkwan, Sriroth, & Oates, 2001), due to the desired properties such as high paste stability (Chatakanonda, et al., 2003; Defloor,

Swennen, Bokanga, & Delcour, 1998). In order to rationally extend the industrial applications of cassava starch, it is necessary to understand the effects of modifications such as glow-plasma on its supramolecular structure and thus its thermal property. However, there have been few studies on how glow-plasma regulates the thermal transition of cassava starch especially from a hierarchical structural view. The lack of this understanding prevents us from comprehensively exploring the mechanism of glow-plasma modification of starch. Therefore, in this study, cassava starch was treated by the oxygen and helium glow-plasmas, respectively, to modulate the gelatinization (thermal transition) through changing the supramolecular structure (semi-crystalline lamellae, crystallites, etc.). The results from the present work would help us in understanding the effects of glow-plasma on the multi-scale supramolecular structure and thus the thermal behavior of cassava starch, as well as the related mechanism.

2. Materials and methods

2.1 Materials

Cassava starch (amylose content ca. 27%) was purchased from Rose Brand Cassava Starch (Thailand). A moisture analyzer (MA35, Satorius Stedim Biotech GmbH, Germany) was used to determine the moisture content (*MC*) of each starch sample. According to the AOAC (1995) method, the contents of ash, moisture, and starch were determined. The chemical composition of the cassava starch was 0.16 ± 0.02% of ash, 13.03 ± 0.39% of moisture and 98.13 ± 0.16% of starch.

2.2 Glow-plasma treatment

Approximately 10 g of starch (dry basis) was loaded into the reactor chamber and treated with the oxygen or helium glow-plasma for different times (30, 45, or 60 min). The glow plasma was realized by using a HPD-2400 plasma installation (Nanjing Suman Electronics Co., Ltd., China) with oxygen or helium gas (2000 Pa) as the atmosphere, operated at 245 V and 1.1 A. The discharge distance applied in the present study was 10 mm and the moisture content of all the samples was ca. 15% before the treatment. Native starch and the modified starch samples were referred to as Cassava, Cassava-O_2-30, Cassava-O_2-45, and Cassava-O_2-60 (Cassava-He-30, Cassava-He-45, and Cassava-He-60), where "O_2" or "He" represents the gas type, and "30" indicates the glow-plasma treatment time.

2.3 Microscopy

A polarized light microscope (Axioskop 40 Pol/40A Pol, ZEISS, Oberkochen, Germany) equipped with a 35 mm SLA camera (Power Shot G5, Canon, Tokyo, Japan) was used. The magnification was 500 (50×10). The starch granules were dispersed as 10 mg starch in 1 mL of distilled water in glass vials. Then, a drop of starch suspension was transferred onto a slide and covered with a cover slip. Both ordinary and polarized light sources were used for observations.

2.4 Small-angle X-ray scattering (SAXS)

The semi-crystalline starch granule is constituted by crystalline and amorphous regions, and its nano scale structure such as the alternating crystalline-amorphous (semi-crystalline) lamella is normally studied by the SAXS technique (Tan, Zhang, Chen, Li, Li, & Xie, 2015; Zhang, et al.,

2015b; Zhang, et al., 2014a; Zu, Zhang, Chen, Xie, Li, & Li, 2016). SAXS measurements were performed according to our previously method (Zhang, et al., 2014b) with proper modification. An SAXSess system (Anton Paar, Austria), operated at 50 mA and 40 kV, using Cu Kα radiation with a wavelength of 0.1542 nm as the X-ray source, was used to collect the data of starch samples treated by the oxygen or helium glow-plasma. The samples were sealed and kept at 20 °C for 24 h before the SAXS measurements to achieve equilibrium samples. The total moisture content of each sample was ca. 60%. Then, each sample was placed in a paste sample cell and was exposed at the incident X-ray beam for 10 min. The data, recorded using an image plate, was collected by the IP Reader software program with the PerkineElmer Storage Phosphor System. The data in the range of ca. 0.12 nm^{-1} $q <$ 1.4 nm^{-1} was used as the SAXS result. All data were normalized, and the background intensity and smeared intensity were removed using the SAXSquant 3.0 software program for further analysis.

2.5 X-ray diffraction (XRD)

The samples were equilibrated at 40 °C for 24 h and the moisture content of all the samples was ca. 10%. XRD analysis was performed on an X'Pert PROX diffractometer (Panalytical, Almelo, Netherlands), operated at 40 mA and 40 kV, using Cu Kα radiation with a wavelength of 0.1542 nm as the X-ray source. Data was obtained at 2θ (θ being the angle of diffraction) of 4-40 ° using sequential scanning with a scanning speed of 10 °/min and a scanning step of 0.033 °. The relative crystallinity (X_c, %) (Tan, Flanagan, Halley, Whittaker, & Gidley, 2007; Zhang, et al., 2015a; Zhang, et al., 2015b) for the starch samples was calculated using the PeakFit software (Version 4.12),

according to Equation (1):

$$X_c = \frac{\sum_{i=1}^{n} A_{ci}}{A_t} \quad (1)$$

where A_{ci} is the area under each crystalline peak with index i, and A_t is the total area of the diffraction pattern.

2.6 Differential scanning calorimetry (DSC)

Thermal transition (e.g., gelatinization) is a crucial process to transform starch into usable form (paste, gel, etc.) (Liu, Xie, Yu, Chen, & Li, 2009), involving three consecutive stages, and thus has a close relationship to the productions of starch-based products. The thermal characteristics of starch samples were investigated using a PerkinElmer DSC Diamond-I with an internal coolant (Intercooler 1P). A constant moisture content of ca. 70% was maintained during DSC measurements by using a high pressure stainless steel pan (PerkinElmer No. B0182901) with a gold-plated copper seal (PerkinElmer NO. 042-191758). About 10 mg of starch sample was used, and then scanned from 50 to 100 °C at a heating rate of 5 °C/min. The onset temperature (T_o), peak temperature (T_p), endset temperature (T_e), and enthalpy (ΔH) of cassava starch gelatinization were recorded. All the results are reported as the averages of 3 replicates and the enthalpy was calculated based on the weight of dry starch.

3. Results and discussion

3.1 Microscopic morphology

When the starch granule is exposed under polarized light, a polarization cross can be observed, corresponding to an anisotropic phenomenon resulting from the orderly arranged starch molecules in crystalline regions and the disorderly arranged starch molecules in amorphous regions . **Fig. 1** and **2** show the polarized light micrographs of cassava starch samples before and after the oxygen or helium glow-plasma treatment. Native cassava starch consists of mainly elliptical granules with some irregular species. The morphology and polarization crosses of cassava starch showed negligible changes after the oxygen or helium glow plasma treatment, indicating that the glow-plasmas could not apparently change the morphological characteristics on the micron scale (e.g., size and integrity) and the spherulitic crystallites in the starch granules. In order to further disclose whether the glow-plasma could modulate the thermal transition properties of cassava starch from a structural view, the changes in the supramolecular structural features (involving lamellar and crystalline structures other than granule morphology) on different length scales during the oxygen or helium glow-plasma treatment were evaluated, which are discussed below.

3.2 Lamellar structure

The double-logarithmic SAXS patterns of cassava starches subjected to the oxygen or helium glow-plasma are presented in **Fig. 3,** in which native cassava starch displayed a typical scattering peak at ca. 0.6 nm^{-1} (*q* value), ascribed to the semi-crystalline lamellar structure. The average thickness (*d*) of the semi-crystalline lamellae was calculated using the Woolf-Bragg equation *d* =

$2\pi/q$ (Pikus, 2005b; Zhang, et al., 2014b), and the *d* value for native cassava starch was 9.905 nm (as presented in **Table 1**). After the oxygen glow-plasma treatment for 30 min, cassava starch showed a slight increase in the thickness of the semi-crystalline lamellae, and no evident change was observed with the increased treatment time; however, when cassava starch was treated by the helium glow-plasma, the lamellar thickness remained unchanged after the 30 min treatment but increased as the time prolonged. This indicates that the helium glow-plasma was probably less effective (than the oxygen glow-plasma) at altering the lamellar structure of cassava starch. In addition, the flawless semi-crystalline lamellae with a high ordering degree result in a scattering peak with fine visibility at ca. 0.6 nm^{-1} (Zhang, et al., 2014c). The cassava starch did not show apparent changes in the lamellar peak visibility after the glow-plasma treatment, which suggests that the perfection and ordering degree of the semi-crystalline lamellae were only slightly affected by the oxygen or helium glow-plasma.

According to the paracrystalline model proposed by Cameron and Donald (Cameron & Donald, 1993a, 1993b), except the value of *d*, other two structural parameters can be acquired for the semi-crystalline lamellae from the SAXS data. That is, the difference in election density between the amorphous lamellae and the amorphous background, $\Delta\rho_u = \rho_u - \rho_a$, where ρ_u and ρ_a are the electron densities of the amorphous background (i.e., the amorphous growth rings) and the amorphous components in the semi-crystalline lamellae, respectively; the difference in electron density between the crystalline and amorphous lamellae, $\Delta\rho = \rho_c - \rho_a$, in which ρ_c is the electron density of the

crystalline regions in the semi-crystalline lamellae. While an increase in $\Delta\rho_u$ has simultaneous effects of raising the low-angle intensity and lowering the definition of the peak without changing the peak position, the main effect of increased $\Delta\rho$ is to increase the overall intensity including the peak intensity. As shown in **Fig. 3A**, decreases in the intensity and in the resolution (i.e., an increase in the width) of the lamellar peak could be observed after the oxygen glow-plasma treatment for 30 min, which was attributed to a decreased $\Delta\rho$ and an increased $\Delta\rho_u$, resulting from the greatest destruction to the crystalline lamellae, the intermediate destruction to the amorphous lamellae and the weakest destruction to the amorphous background materials. Nevertheless, with the prolonged treatment time of oxygen glow-plasma, the lamellar peak resolution (width) showed no evident changes, whereas slight reductions in the intensities of the scattering peak and the low q range were presented. This indicates that when the treatment time was longer than 30 min, the oxygen glow-plasma induced more prominent destruction to the crystalline lamellae than to the amorphous lamellae, together with similar alterations to the amorphous lamellae and the amorphous background, leading to further decreased $\Delta\rho$ but relatively stable $\Delta\rho_u$.

When the helium glow-plasma was used, the treatment for 30 min resulted in the most intense destruction to the crystalline lamellae, the intermediate destruction to the amorphous lamellae, and the weakest destruction to the amorphous background. This reduced $\Delta\rho$ but increased $\Delta\rho_u$ for the cassava starch, as confirmed by decreases in the intensity and the resolution of the lamellar peak and an increase in the intensity at low q values. As the treatment time increased, the helium glow-plasma

tended to induce more prominent alterations to the crystalline lamellae than those to the amorphous lamellae, while the amorphous background also suffered more intense changes than did the amorphous lamellae. As a result, both $\Delta\rho$ and $\Delta\rho_u$ of the cassava starch were reduced by the helium glow-plasma, allowing a better resolution (narrowed width) for the lamellar peak, and decreases in the intensities of the peak and the low q range. In addition, by comparing the results in **Fig. 3A** with those in **Fig. 3B**, it was found that a more apparent intensity reduction in the small-angle range (q values smaller than lamellar peak position) was induced by the oxygen glow-plasma rather than the helium glow-plasma, which again confirmed the stronger ability of the glow-plasma with oxygen atmosphere to influence the lamellae and the background materials.

3.3 Crystalline structure

Based on the arrangements of the double-helices of amylopectin side chains and the amylose single-helices, the crystalline structure of starch is classified as A-, B-, C- or V-type (Buleon, et al., 1998; Gernat, Radosta, Damaschun, & Schierbaum, 1990; Kim, et al., 2010), which can be accurately characterized by the WAXS and XRD techniques (Tan, et al., 2015; Zhang, et al., 2015a; Zhang, et al., 2015b; Zhang, et al., 2014b). The XRD patterns of cassava starches before and after the oxygen or helium glow-plasma treatment are shown in **Fig. 4**, where the crystalline regions (long-range orders) in the starch granule show sharp peaks and the amorphous materials exhibit a dispersive scattering pattern. Apparently, the cassava starch in present work displayed a typical A-type polymorphic structure with main scattering peaks at approximately 15 °, 17 °, 18 °, and 23 °

(2θ), and the crystalline type kept unchanged after the oxygen or helium glow-plasma treatment. For further disclose how the glow-plasma changed the crystalline characteristics of the cassava starch, the relative crystallinity (X_c), i.e., the ratio for the area of scattering peaks to the total area under the XRD pattern, was calculated, and the results are summarized in **Table 1**. The X_c for native and 60 min oxygen glow-plasma treated cassava starches was 45.78% and 42.68%, respectively, accompanied by X_c values somewhere between them for other starch samples. This was consistent with the SAXS results that the crystalline lamellae could be affected by the glow-plasmas. Also, the oxygen glow-plasma could more intensely destroy starch crystallites than could do the helium glow-plasma (see **Table 1**). The long-range scale crystallites are mainly comprised of monoclinic and/or hexagonal crystal units, containing short-range double-helices and inter-helical water molecules which are organized together through a large number of inter- and intra-molecular hydrogen bonds (Perez & Bertoft, 2010; Zhang, et al., 2015b). Hence, we suggest that the changes of starch crystallites during the treatment were caused by the breakage of the hydrogen bonding network at the molecular level by the glow-plasmas.

3.4 Thermal behavior

Fig. 5 shows the DSC thermograms of native cassava starch and its modified samples with the oxygen or helium treatment, and **Table 1** records the related thermal parameters. All starches displayed a typical endotherm in the temperature range of ca. 65-75 °C, due to the melting of predominantly amylopectin crystallites in the cassava starch granules (Zhang, et al., 2015a; Zhang, et

al., 2015b). While both oxygen and helium glow-plasmas could increase the thermal transition temperatures and reduce the enthalpy (related to the less starch crystallites, as shown by X_c in **Table 1**), this phenomenon became more evident as the treatment time increased. Specifically, the onsite gelatinization temperature (T_o) and enthalpy (ΔH) of native cassava starch were 65.09 °C and 15.221 J/g, respectively; these two values changed to 66.96 °C and 12.616 J/g for Cassava-O_2-60 and to 66.47 °C and 14.466 J/g for Cassava-He-60. This indicates that compared to the helium glow-plasma, the oxygen glow-plasma was more powerful at altering the thermal property of cassava starch, which was similar to the changing trends of the SAXS and XRD results. Again, the gelatinization temperature range of cassava starch could be narrowed by the glow-plasmas (especially with the oxygen gas) and gradually reduced with the increased treatment time.

3.5 Structure-thermal property relationship

As revealed by our very recent studies (Zhang, et al., 2015a; Zhang, et al., 2014a), the nitrogen and helium glow-plasmas induced disorganization in the aggregation structures of potato starch, and eventually caused reductions in its thermal transition temperatures and enthalpy in abundant water; oxygen glow-plasma could disorganize the supramolecular structure of potato and corn starches. However, in the present study, although the glow-plasmas reduced the ordering of the supramolecular hierarchical structure and the transition enthalpy for the cassava starch, the thermal transition temperatures increased after the glow-plasma treatment, and with the increased treatment time, a decreased transition temperature range was observed. This unexpected phenomenon has

never been found for plasma-treated starch products, which led us to disclose the structure-property relationship (i.e., the underlying mechanism) for the glow-plasma treated cassava starch, based on the gelatinization principle (Gallant, Bouchet, & Baldwin, 1997; Liu, et al., 2009; Zhang, et al., 2014b) and the glow-plasma induced changes in starch.

Since the enthalpy of the thermal transition reflects the amount of starch molecular orders (long-range crystallites, double- and/or single- helices, etc.) melted during the hydrothermal treatment, we propose that the reduction in the gelatinization enthalpy resulted from the supramolecular structural disorganization on different length scales. To be more specific, during the thermal transition of cassava starch, the elevated temperature gradually promoted water molecules to penetrate into the granules to break the inter- and intro-molecular hydrogen bonds for disrupting the starch orders. Thus, the glow-plasma induced destructions to the lamellar and background regions on the nano scale (see **Fig. 3**) and to the long-range crystallites (cf. **Fig. 4** and **Table 1**), which resulted in a decrease in the melting enthalpy (**Table 1**). Nonetheless, these multi-scale structural disruptions did not weaken the thermal stability of cassava starch. Our previous study (Zhang, et al., 2015a) has shown that, as potato starch with the B-polymorph had open packing of helices in each hexagonal crystal unit with 36 inter-helical water molecules, this packing could be induced by the nitrogen and oxygen glow-plasmas. Therefore, weakened packing of overall molecular orders (crystallites, and double- and single-helices) could result in decreased thermal resistance of starch (i.e., reduced transition temperatures). However, for the cassava starch here, the typical A-type crystalline

structure contained tightly packed double-helices with only 8 water molecules in each monoclinic crystal unit, which made it difficult for the oxygen and helium glow-plasmas to reduce the perfection of the long- and short-range molecular orders. Consequently, the glow-plasmas tended to mainly disrupt the ordering components with relative low perfection (i.e., low thermal stability) of cassava starch, as elucidated by the destructions to partial crystallites and the double-helices aligned in the crystalline lamellae (see **Fig. 3** and **4,** and **Table 1**). The related schematic representation for the glow-plasma effects on cassava starch is shown in **Fig. 6**. This eventually enhanced the thermal resistance of the glow-plasma modified cassava starch, accompanied with decreased crystallinity (X_c in **Table 1**). This predominant amorphization of starch orders with low thermal stability originally shown in the initial gelatinization temperature range expectedly reduced the transition temperature range of cassava starch.

Additionally, the oxygen glow-plasma shows strong oxidizing ability to even induce molecular degradation of starch (Zhang, et al., 2014a), whereas the helium glow-plasma is relatively mild to polymerize starch molecules (Zhang, et al., 2015a). Consistent with this fact, more drastic alterations occurred in the supramolecular hierarchical structure (i.e., lamellae, amorphous background and crystallites) of the oxygen glow-plasma treated cassava starch than in the structure of the helium glow-plasma modified ones. Thus, the thermal transition parameters of cassava starch could be more effectively regulated by the oxygen glow-plasma.

4. Conclusion

The oxygen and helium glow-plasmas have been confirmed to be capable of changing the thermal behavior of cassava starch by inducing disruptions in the multi-scale supramolecular structure. Specifically, although negligible changes in the granule morphology were observed, the crystallites with low perfection and thermal stability were preferably disorganized by the glow-plasmas, leading to decreases in the electron density different between the crystalline and amorphous lamellae, the relative crystallinity and the transition enthalpy, and increases in the transition temperatures, together with a narrowed transition temperature range. The thermal behavior of cassava starch could be further regulated by changing the gas type and the treatment time. These findings are much different from previous work which showed if glow-plasma led to disorganization in the supramolecular structure of starch, the thermal transition temperatures would be reduced. The underlying mechanism was explored by proposing a structure-thermal property relationship for glow-plasma treated cassava starch. Therefore, from a supramolecular structural view, this study enables a good understanding of how glow-plasma modulates the thermal transition property of cassava starch, which is of value for rational development of glow-plasma modified starch with controlled thermal behavior for various food and non-food products. As the main effect of glow-plasma is to disorder the starch structures on multiple scales, this work is also valuable for the design of starch-based products with tailored thermal behavior using other physicochemical processes such as heat-moisture treatment which can also disorganize the starch hierarchical structure.

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Conflict of interest statement

The authors have declared no conflict of interest.

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Industrial relevance:

Glow-plasma is a non-thermal physical technique and has gain huge interest in polymer modification due to the concerns over generated wastes and safety issues resulting from chemical modification. As the major storage carbohydrate in higher plants, starch is one of the most important raw materials for food and non-food industries. To improve the performance of starch and extend its applications, it is indispensible to understand how a specific technique alters the structure-property of starch. Regarding this, the present work revealed that the oxygen or helium glow-plasma preferably disorganized the crystallites of cassava starch with low perfection and thermal stability, which resulted in decreases in the relative crystallinity and the transition enthalpy but increases in the transition temperatures together with a narrowed transition temperature range. The thermal behavior of cassava starch could be further regulated by changing the gas type and the treatment time. These findings are much different from previous work which showed if glow-plasma disorganized the supramolecular structure of starch, its thermal transition temperatures would be reduced. Hence, this study enables a understanding of how glow-plasma modulates the thermal property of cassava starch from a structural view, which is of value for rationally using glow-plasma as a new method to regulate the thermal transition of starch, for the production of starchy food products with desired thermal behavior.

Figure Captions

Fig. 1 Ordinary and polarized light micrographs (500 ×) of cassava starch granules before and after the oxygen glow-plasma treatment for different times.

Fig. 2 Ordinary and polarized light micrographs (500 ×) of cassava starch granules before and after the helium glow-plasma treatment for different times.

Fig. 3 Double-logarithmic SAXS patterns of cassava starch samples before and after the oxygen (A) or helium (B) glow-plasma treatment for different times.

Fig. 4 XRD patterns of cassava starch samples before and after the oxygen or helium glow-plasma treatment for different times.

Fig. 5 DSC thermograms of cassava starch samples before and after the oxygen or helium glow-plasma treatment for different times.

Fig. 6 Schematic representation for the structural changes of cassava starch subjected to the glow-plasma treatment.

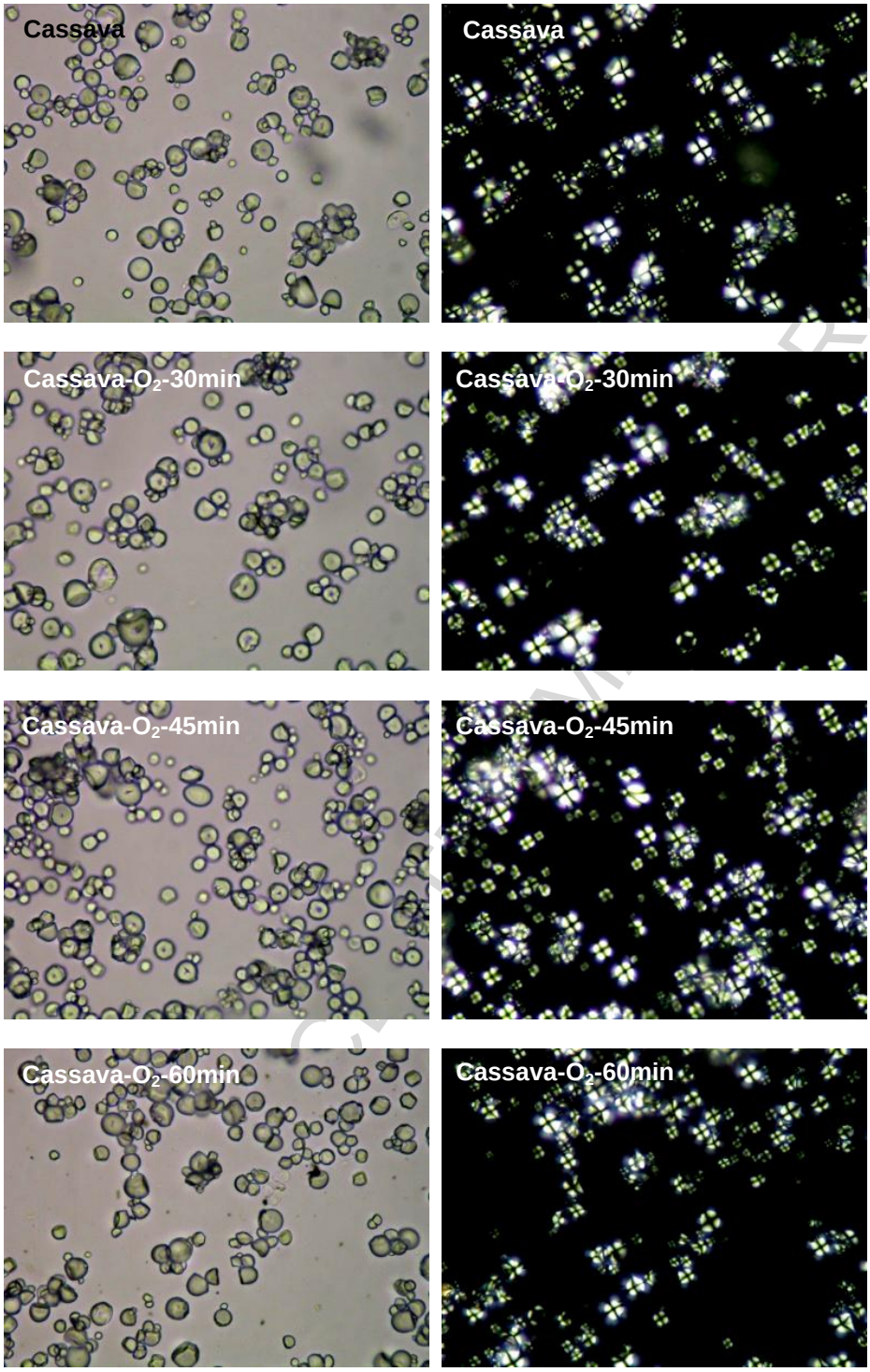

Fig. 1

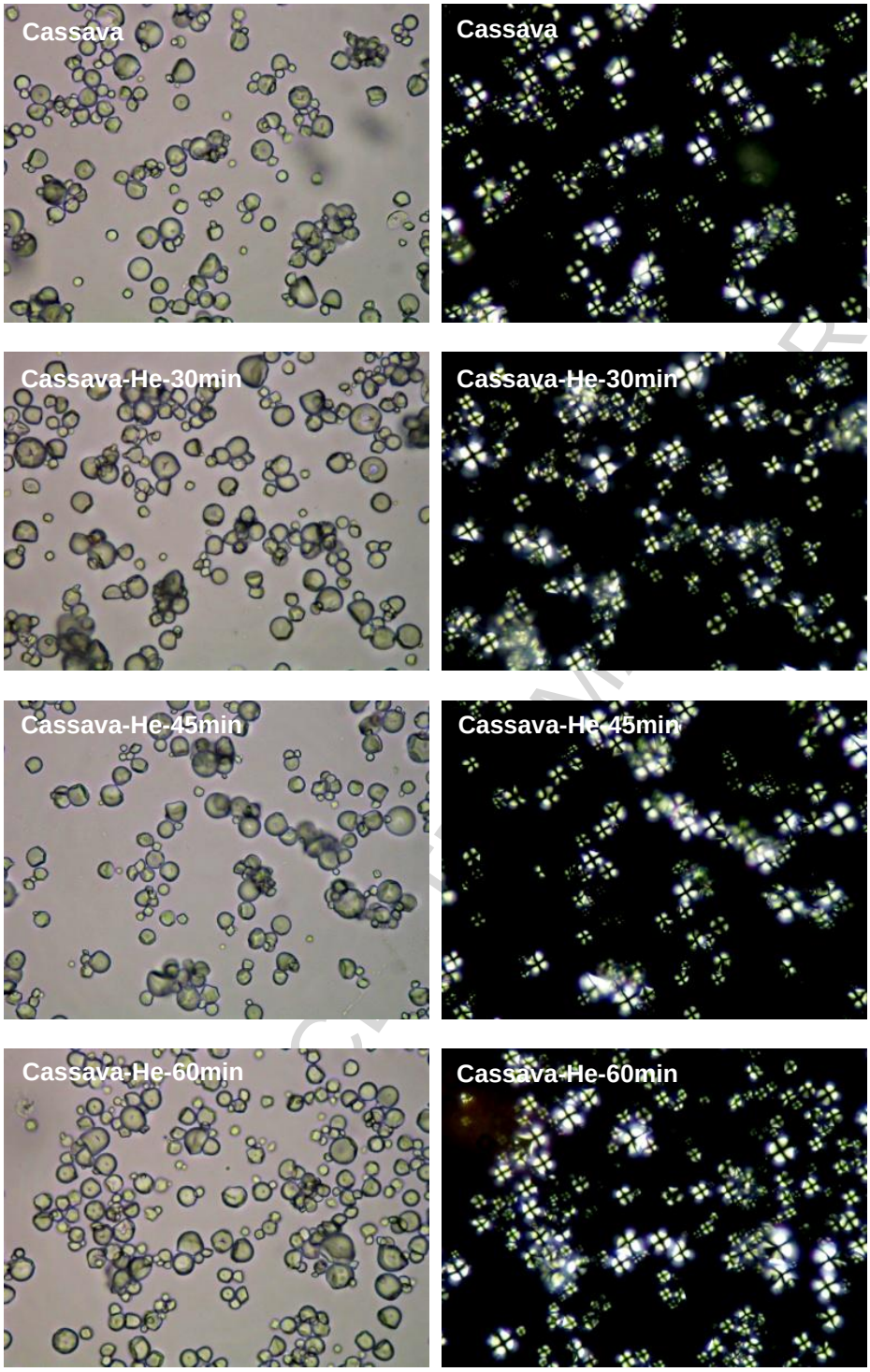

Fig. 2

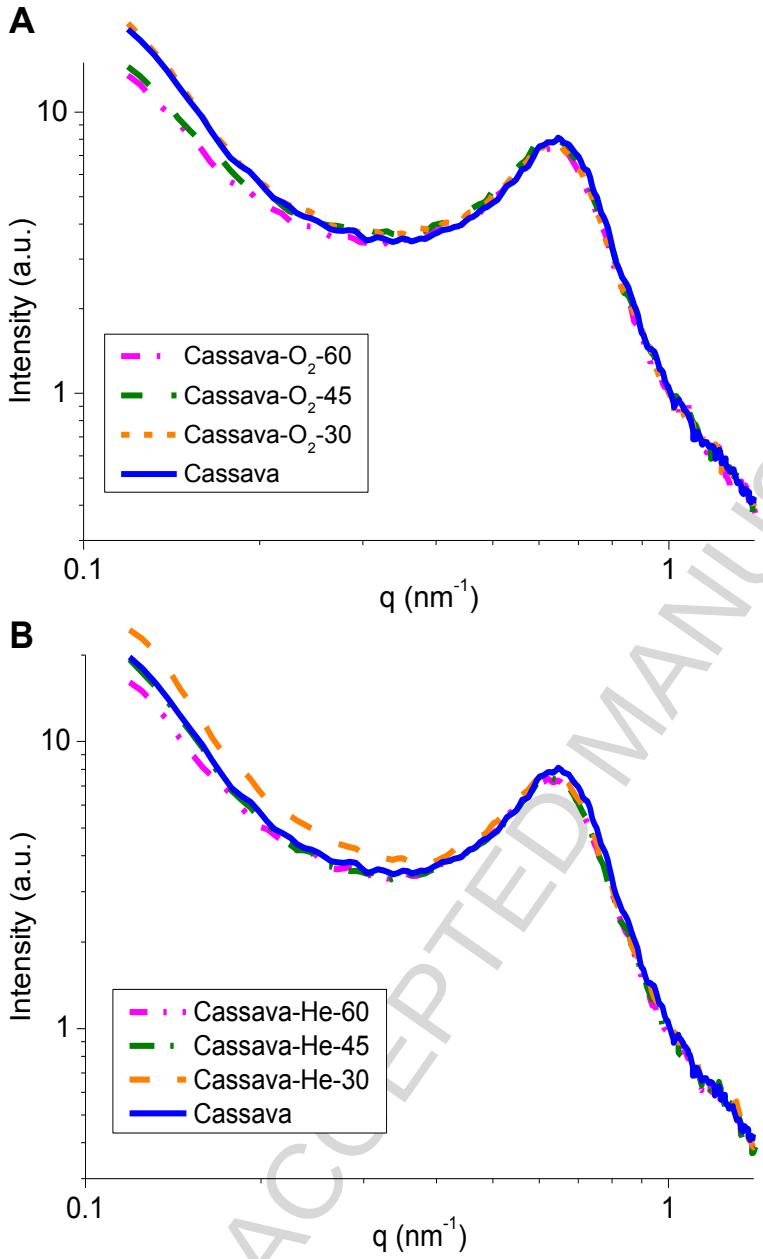

Fig. 3

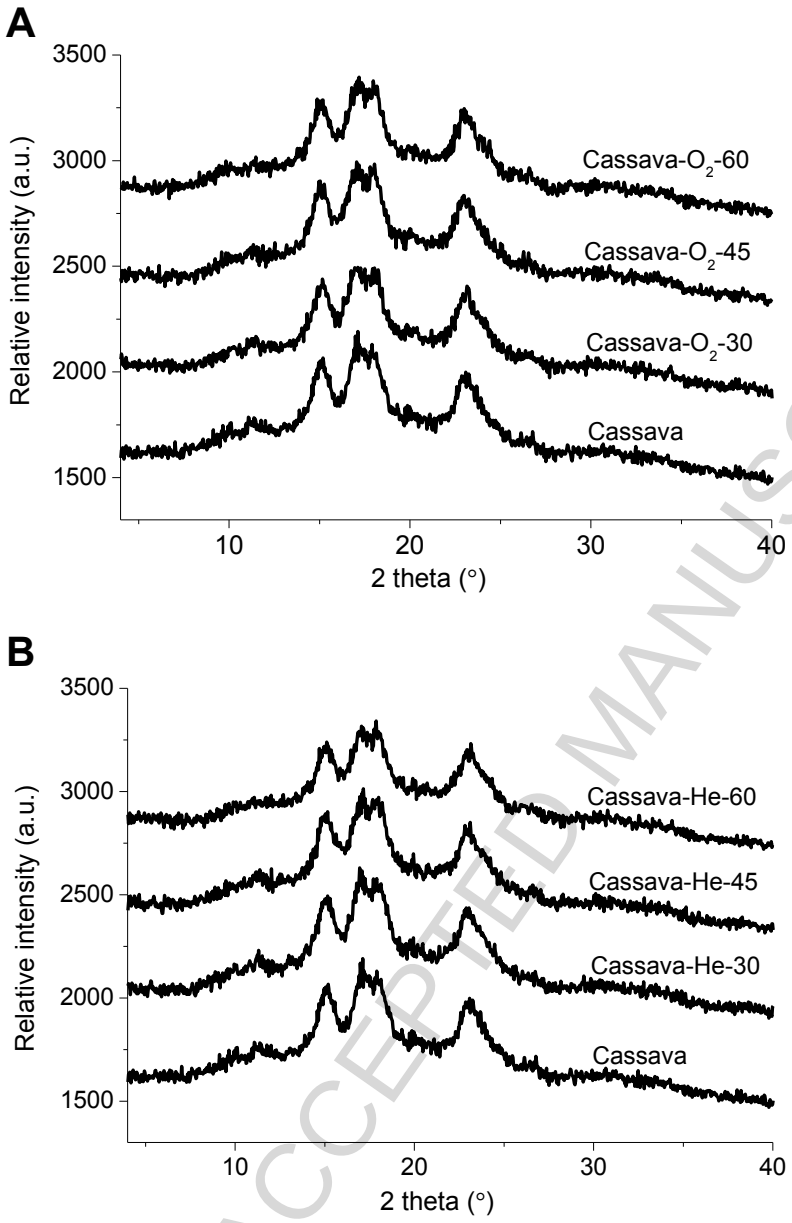

Fig. 4

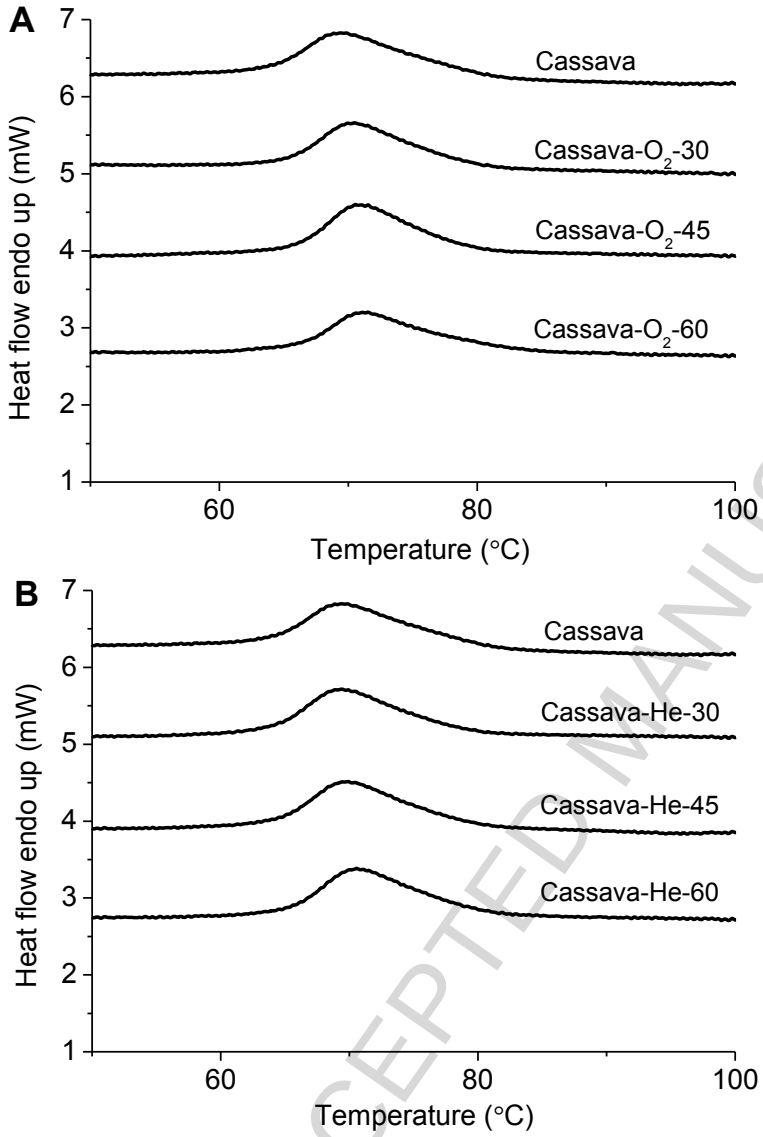

Fig. 5

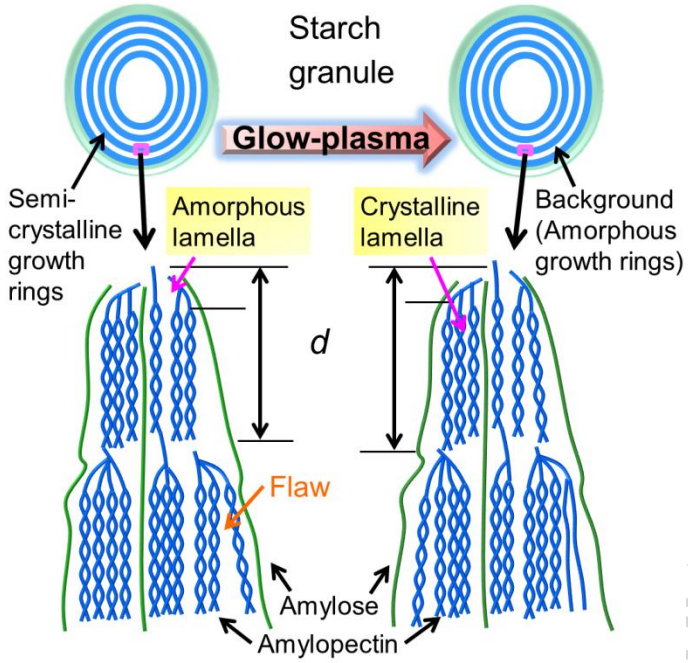

Fig. 6

Table 1 Lamellar, crystalline, and thermal transition parameters of cassava starch samples before and after oxygen (O_2) or helium (He) glow-plasma modification for different times [A]

	Cassava	Cassava - O_2-30	Cassava - O_2-45	Cassava - O_2-60	Cassava - He-30	Cassava - He-45	Cassava - He-60
q (nm^{-1})	0.634	0.627	0.627	0.627	0.634	0.627	0.621
d (nm)	9.905	10.016	10.016	10.016	9.905	10.016	10.113
X_c (%)	45.78	44.96	44.70	42.68	45.11	44.64	43.76
T_o (°C)	65.09	66.49	66.72	66.96	65.77	65.88	66.47
T_p (°C)	69.48	70.41	70.57	71.49	69.32	69.90	70.57
T_e (°C)	75.52	75.82	76.27	76.46	76.11	76.13	76.49
ΔT (°C)	10.43	9.33	9.55	9.50	10.34	10.25	10.02
ΔH (J/g)	15.221	13.506	13.191	12.616	15.001	14.683	14.466

[A] Lamellar parameters measured by SAXS: q, the peak position of semi-crystalline lamellae; d, the average thickness of semi-crystalline lamellae. Parameter obtained by XRD: X_c, the relative degree of crystallinity. Gelatinization parameters measured by DSC: T_o, onsite temperature;T_p, peak temperature;T_e, endset temperature; ΔT, gelatinization range ($T_e - T_o$).

Highlights

►From a structural view, glow-plasma effects on starch thermal behavior were explored.

►Glow-plasma degraded starch crystallites with low perfection and thermal stability.

►Glow-plasma increased the transition temperature values of cassava starch.

►Glow-plasma narrowed the gelatinization temperature range of cassava starch.

►Glow-plasma can serve as a technique to modulate starch thermal property.